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High strength - high conductivity silver nanowire-copper composite wires by spark plasma sintering and wire-drawing for non-destructive pulsed fields

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Abstract— New Ag-Cu composite wires are developed for the winding of non-destructive pulsed magnets. Silver nanowires were mixed with a micrometric copper powder. Copper and 1, 5 and 10 vol. % silver-copper cylinders were prepared by spark plasma sintering. They served as starting materials for room temperature wire-drawing, enabling the preparation of conducting wires containing copper ultrafine elongated grains and silver nanowires located at the grain boundaries. The tensile strength at 293 K and 77K for the composite wires is more than twice those for the corresponding pure copper wires. The electrical resistivity is however increased and we show that the composites containing only 1 vol. % silver offer the best compromise.

Index Terms— copper; silver nanowires; spark plasma sintering; wire-drawing; nanostructured conductors

I. Introduction

THE generation of high pulsed magnetic fields higher than 60 T requires the use of coils wound with high conductivity wires to limit the heating, and very high mechanical strength to be able to resist the Lorentz forces. Indeed, Lorentz forces induce in the wires a von Mises stress of 1 GPa at B = 60 T and higher than 2.2 GPa at B = 100 T [1], [2]. LNCMI-Toulouse produces some of the most intense non-destructive pulsed magnetic fields in the world with a European record of 98.8 T [3]

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and aims at reaching more than 100 T. The best way to combine high mechanical strength and high electrical conductivity is the cold drawing of copper-based composite wires such as Cu/Nb [4] and carbon nanotube (CNT)-Cu [5], [6] wires. Cu/CNT wires were prepared through a collaboration between the Laboratoire National des Champs Magnétiques Intenses and the Centre Inter-universitaire de Recherche et d'Ingénierie des Matériaux. Their preparation combines the mixing of copper and CNT in order to form a homogeneous composite powder, the cylinder-shaped consolidation of this powder by Spark Plasma Sintering (SPS) and the drawing at room temperature of the so-obtained cylinder into progressively finer wires. The wires have a high mechanical strength for a content of only 1% of carbon, due to the presence of the CNT second phase and the ultrafine microstructure of the copper matrix [5]. The finer Cu-CNT wires reach a value of Ultimate Tensile Strength (UTS) of 740 MPa (at 77 K), with an electrical resistivity of 0.41 μΩ.cm (at 77 K). For this work, we decided to replace the CNTs by 1D silver nanowires (NWs) in order to further increase the mechanical strength. It is worth noticing that is the first attempt to develop Ag/Cu *composite* wires whereas Ag/Cu (6-24 % wt. Ag) *alloyed* wires have been developed by metallurgy routes (melting, solidification and drawing). The latter wires show a very high UTS (1160 MPa) but a high electrical resistivity (ρ = 0.81 μΩ.cm) [7]-[10] at 77 K.

II. Materials: fabrication and microstructure

The Ag NWs (30-60 μm long and 200-300 nm in diameter) were synthesized by reducing $AgNO_3$ with ethylene glycol in the presence of poly (vinyl pyrrolidone) as described by Sun et al. [11]. The Ag NW-Cu composite powders (1, 5 and 10 % vol. Ag, i.e. 1.2, 5.8 and 11.5 % wt. Ag) were prepared by pouring the appropriate amounts of Cu powder into the Ag NWs suspension in ethanol under sonication. When a homogeneous suspension is obtained, ethanol is evaporated (rotary evaporator, 80 °C). The powders are reduced under H_2 atmosphere to remove any copper oxide present on the surface of the copper grains. This reduction step also aims at obtaining a pre-sintered powder, because it was observed that this state was necessary to perform the wire-drawing without break-up. The increase in silver content induces an increase in the reduction

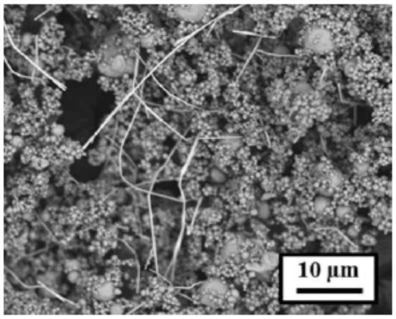

Fig. 1. SEM image of the Ag–Cu powders containing 1 vol% Ag.

temperature in order to obtain a pre-sintered powder. The 1, 5 and 10 vol. % Ag powder was heated at 160, 230 and 280 °C. The powder
shows a homogeneous distribution of the silver microwires between the copper grains (Fig. 1). Cu and Ag-Cu cylinders, 8 mm in diameter and 33 mm in length were sintered by SPS (PNF²-Toulouse, Dr. Sinter 2080, SPS Syntex Inc., Japan) in a WC/Co die. Technical details on the process and procedure were explained in [12]. The Ag-Cu powders were sintered at 500 °C except the powder containing 1 vol. % Ag which was sintered at 400 °C where the Ag solubility limit in Cu is below 0.1 vol. %. These samples are named XAg-Cu/YYY hereafter, where X corresponds to the silver content in volume percent and YYY to the sintering temperature. A 1Ag-Cu/400 cylinder is shown in Fig. 2a. The cylinders have a densification equal to 94 ± 2 % (higher densifications hamper wire-drawing). The microstructure of the cylinders was investigated by scanning electron microscopy (SEM, JEOL JSM 7100 TTLS LV, operated at 10 kV) equipped with an electron backscattered diffraction (EBSD) camera (NordlysNano, Oxford Instruments) and energy dispersive X-ray spectrometry (EDS: Xmax 80mm², Oxford Instruments). The phase map for a transverse section (Fig. 2b) shows dispersed Ag grains (colored in red) in Cu grains (colored in green) for 1Ag-Cu/400. Cu have not grown significantly during sintering, in fact the size of the copper grains (d10 = 0.40 µm; d50 = 0.91 µm; d90 = 1.88 µm, particle size distribution d10, d50, and d90 corresponding to the percentages 10%, 50%, and 90% of particles under the reported particle size) and the silver grains (d10 = 0.22 µm; d50 = 0.27 µm; d90 = 0.40 µm) are very close to their respective size in the initial powders. The cross-sectional areas of the cylinders were decreased by wire-drawing at room temperature. The sample is drawn through conical WC dies, forming progressively finer wires. Wire samples (1 - 0.2 mm in diameter and 340 mm in length) are taken between wire-drawing passes in order to perform the microstructural, mechanical and electrical characterizations. An Ag-Cu wire 0.2 mm in diameter is shown in Fig. 3a. The microstructure of the 0.5 mm diameter 1Ag-Cu/400 wire was investigated by EBSD. The phase map of the longitudinal-section (Fig. 3b) shows the Ag grains (colored in red) were dispersed along the grain boundaries of Cu (colored in green). The grains size map (Fig. 3c) shows that the Cu and Ag grains are ultrafine and with a relatively narrow distribution (d10 = 0.14 µm; d50 = 0.20 µm; d90 = 0.32 µm for Cu and d10 = 0.14 µm; d50 = 0.17 µm; d90 = 0.21 µm for Ag) and that they are elongated by several micrometers along the drawing axis.

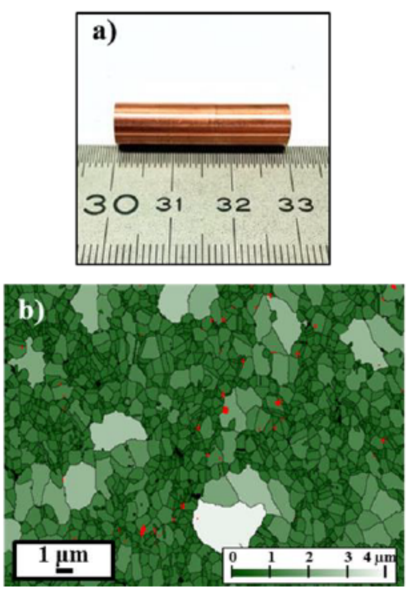

Fig. 2. (a) photography of a cylinder, (b) EBSD phase maps of the transverse section showing copper grains (shades of green depending on the grains size) and silver grains (red) for 1Ag-Cu/400 cylinder.

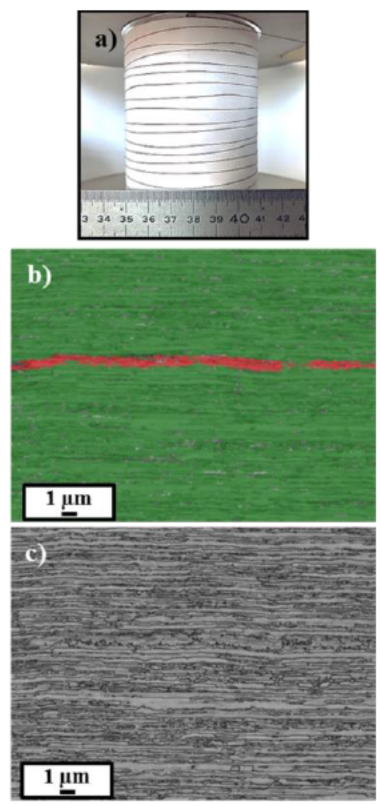

Fig. 3. (a) photography of the Ag-Cu 0.2 mm diameter wire, (b) EBSD phase maps of the longitudinal section showing copper grains (green) and silver grains (red), (c) EBSD grains maps of the longitudinal section for 1Ag-Cu/400 0.5 mm diameter wire.

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III. Electrical Characterization

The electrical resistivity of the wires was measured at 293 K and 77 K for different wire diameters (D) using the four-probe method with a maximum current of 100 mA to avoid heating the wires. Tab I shows the conductor resistivity as a function of wire diameter D and temperature.

TABLE I
Electrical resistivity versus wire diameter at 293 K and 77 K for the different wires.

	Resistivity (μΩ.cm)							
D	**Cu/600**		**1Ag-Cu/400**		**5Ag-Cu/500**		**10Ag-Cu/500**	
(mm)	**293 K**	**77 K**	**293 K**	**77 K**	**293 K**	**77 K**	**293 K**	**77 K**
1.0	1.82	0.27			2.07	0.53	2.05	0.53
0.8	1.81	0.27	1.94	0.42	2.08	0.55	2.06	0.55
0.6	1.83	0.28	1.97	0.44	2.14	0.59	2.11	0.57
0.5	1.80	0.28	1.95	0.45	2.12	0.60	2.12	0.60
0.4	1.82	0.28	2.01	0.47			2.16	0.64
0.3	1.84	0.29	2.01	0.49	2.33	0.72	2.22	0.71
0.2	1.84	0.30	2.02	0.51			2.29	0.77

The electric resistivity is in the range 1.82 - 2.33 μΩ.cm at 293 K and in the range 0.27 - 0.77 μΩ.cm at 77 K. The lower resistivity at 77K is due to the fact that the electron-phonon interactions are negligible at cryogenic temperatures. Moreover, for a given sample, the electrical resistivity increases when the diameter of the wire decreases. This reflects the refinement of the microstructure during drawing. Indeed this induces an increase in the density of grain boundaries, which are scattering points for conduction electrons. For Ag-Cu composite wires, the presence of Ag / Cu interfaces causes an increase in electrical resistivity compared with pure copper wires (0.27 - 0.30 μΩ.cm for pure Cu wires and 0.42 - 0.77 μΩ.cm for composite wires at 77 K). A saturation effect is noted because upon the increase in silver content from 5% to 10% there are no more Cu / Ag interfaces but rather larger silver domains [12].

IV. Mechanical Characterization

Tensile tests (INSTRON 1195 machine) were performed at 293 K and 77 K on 170 mm long wires. Precise stresses were measured by the stress gauge system (1000 N or 250 N, 1.6 x 10-5 m.s-1). Tab. II shows UTS as a function of wire diameter D and temperature. The dislocation motion is reduced at low temperature compared to 293 K, resulting in higher UTS values at 77 K (574-1373 MPa) than at 293 K (389-1053 MPa). The dislocation motion is slowed down by the grain boundaries, thus the refinement of the microstructure (and therefore the increase in the density of grain boundaries) results in an increase in the UTS upon the decrease in wire diameter. The presence of the Ag / Cu interfaces also implies an increase of the strength for the composite wires (924-1373 MPa at 77 K) compared to the pure Cu wires (574-605 MPa at 77 K). The UTS values of 10Ag-Cu/500 exhibit the same saturation effect observed for electrical resistivity.

TABLE II
Ultimate Tensile Strength versus wire diameter at 293 K and 77 K for the different wires.

	UTS (MPa)							
D	**Cu/600**		**1Ag-Cu/400**		**5Ag-Cu/500**		**10Ag-Cu/500**	
(mm)	**293 K**	**77 K**	**293 K**	**77 K**	**293 K**	**77 K**	**293 K**	**77 K**
1.0	389	574			667	963	773	1004
0.8	388	588	756	924	847	1062	831	1044
0.6	457	584	795	981	906	1129		1079
0.5	474	597	809	1006	958	1215	943	1106
0.4	484	585	833	1038				
0.3	487	450	887	1109		1215	1053	1373
0.2	503	605	914	1138				

V. Discussion

Fig. 4 shows UTS versus electrical resistivity for the present Ag-Cu composite wires, CNT-Cu composite wires prepared by the same route [5], [6] and Ag/Cu alloyed wires [8]-[10] at 293 K and at 77 K. If we compare the two types of composites, the 1Ag-Cu/400 shows the best UTS values (924 MPa for 1Ag-Cu/400 vs. 744 MPa for 1CNT-Cu). The higher reinforcement with Ag microwires could be explained at least partly from the totally different nature of the CNT/Cu and Ag/Cu interfaces, which warrants further studies. 1Ag-Cu/400 composite wires are also comparatively better than alloyed wires containing 20 times more silver. Indeed, for similar UTS (980 MPa for 1Ag-Cu/400 vs. 938 MPa for Ag-Cu alloy) the resistivity at 77 K of 1Ag-Cu/400 is about 38 % lower (0.44 μΩ.cm for 1Ag-Cu/400 vs. 0.71 μΩ.cm for Ag-Cu alloy). This very good UTS / electrical resistivity compromise for Ag-Cu composites can be explained by the nanostructuration of the copper matrix and the silver second phase which gives the high mechanical resistance. The low silver content and the pure copper matrix which ensure the conservation of a high electrical conductivity could make these wires good candidates for the generation of high pulsed magnetic fields higher than 100 T. They could also find use in DC magnetic field generation. Resistive DC magnets are constructed from Ag/Cu alloy containing 5.7% wt. Ag [13]. At 293 K the properties of this alloy after heat treatment at 350 ° C for 4 hours are: UTS = 550 MPa and ρ = 1.86 μΩ.cm. For a similar resistivity, 1Ag-Cu/400 presents a 38 % higher mechanical strength: UTS = 756 MPa and ρ = 1.94 μΩ.cm.

VI. Conclusion

Here, we present composite wires made up of Ag nanowires dispersed into a Cu matrix. They were prepared by room-temperature wire-drawing of cylinders consolidated by spark plasma sintering. Nanostructuring of the Cu matrix and Ag wires reinforcement gives high strength composite wires. Low sintering temperature (Ag solubility limit in Cu is below 0.1 vol. % at 400 °C so the Cu matrix stays unalloyed) and low silver content ensures high conductivity. The wires containing

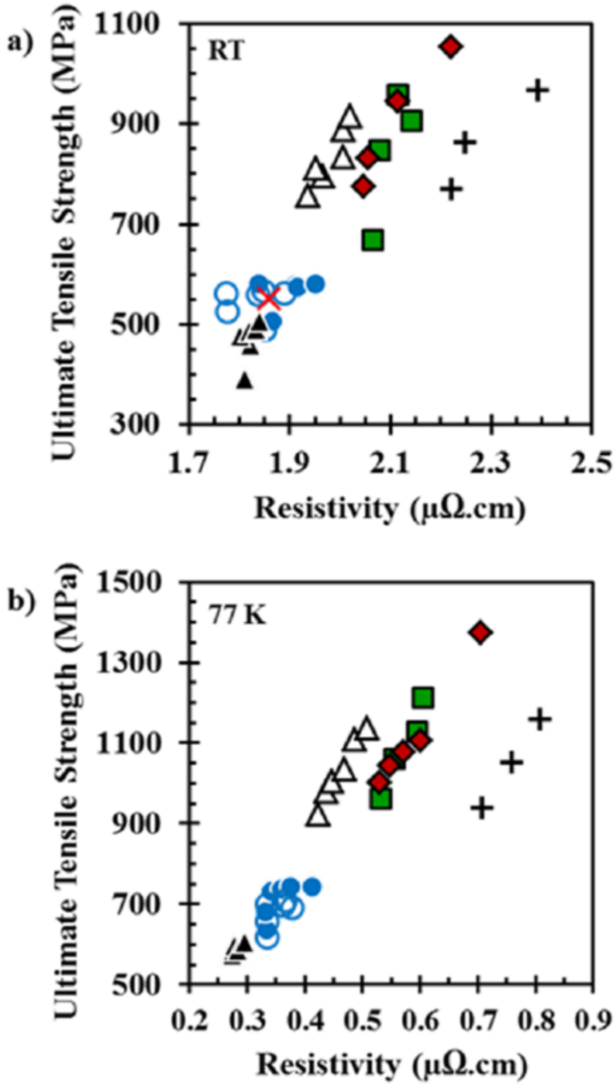

Fig. 4. Ultimate tensile strength versus electrical resistivity for a selection of the present Cu (▲) and 1Ag-Cu/400 (△), 5Ag-Cu/500 (■), 10Ag-Cu/500 (◆), CNT-Cu wires (1 % vol. CNT) [○,●][5][6], Ag-Cu alloy wires (24 - 28 % wt. Ag) (+)[8]-[10], Ag-Cu cold spray alloy (5.7 % wt. Ag) (×)[13], (a) at 293 K and (b) at 77 K.

only 1 vol% Ag offer the best combination of high strength (1100 ± 100 MPa at 77 K) and low electrical resistivity (0.50 μΩ.cm), which could make them good candidates for the development of pulsed or DC magnets. This could be confirmed with the fabrication of magnet prototypes, enabled by a scaling-up of the samples production.

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